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Effects of Boronizing Treatment on Corrosion Resistance of 65Mn Steel in two Acid Mediums

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Abstract

To explore the soil workability of rotary blade suitable for large tilling depth (over 20cm) manufactured through boronizing treatment, this work focuses on the corrosion behavior of 65Mn steel after boronizing treatment in two acid mediums, i.e. the strong acidic medium that hydrochloric solution and the weak acidic that fertilizer-containing soil, and the comparison with existing technology of general rotary blade (lonnealing after overall quenching). The result shows that the corrosion resistance in the two acid mediums of 65Mn steel after boronizing treatment is remarkably improved. After 168 hours' corrosion in the hydrochloric acid solution, the weight loss of boronizing-status sample is only 27.9% of that of lonnealing-status sample. Moreover, there is no obvious weight loss in boronizing-status sample after 168 hours' corrosion in the fertilizer-containing soil, while the weight of lonnealing-status sample is lighter than the original weight after about 150 hours' corrosion. The improvement of the corrosion resistance lies in the significant reduction of the anodization speed in strong acid medium and the effective prevention of phosphorization reaction in weak acidic medium.

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Keywords: boronizing treatment; 65Mn steel; corrosion resistance; acid medium; rotary blade for large tilling depth

1. Introduction

Rotary tillage machinery for large tilling depth (over 20cm) is the basic equipment to implement "cultivation by returning straws completely to fields", a policy for sustainable agricultural development, and the key lies in corresponding rotary blade (Wu et al., 2009). 65Mn steel, featured with favorable comprehensive mechanical

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properties, is listed in the national standard as a specified material for rotary blade by GB/T 5669-2008. However, the existing manufacturing technology of general rotary blade (lonnealing after overall quenching) can not meet the hard-surface and tenacious-core performance requirements of 65Mn steel rotary blade suitable for large tilling depth rotary tillage. Therefore, the manufacturing technology applicable to 65Mn steel deep-tillage rotary blade is one of the urgent key problem in modern agricultural machinery manufacturing.

Boronizing treatment, as a surface chemical heat treatment technology with excellent engineering adaptability, has been widely applied to modification on wear and corrosion resistance of tools, dies, parts and components. Nevertheless, those treated by boronizing mostly are the mild or medium carbon steels such as Q235A steel and 45 steel, while high carbon steels are rarely subject to surface modification through boronizing treatment (Uslu et al., 2007), (Kayali and Yalçin, 2011), (Mathew and Rajendrakumar, 2011), (Su et al., 2009). Wang et al. (2011), aiming at meeting the hard-surface and tenacious-core performance requirements of deep-tillage rotary blade, introduce boronizing treatment into rotary blade manufacturing to replace the original heat treatment technology of lonnealing after overall quenching, to have the surface covered with highly-hard boronizing layer to meet its wear resistance. At the same time, the core is still provided with pearlite microstructure with the favorable comprehensive mechanical property to satisfy requirement of bending strength, which may solve the aforesaid technical problem with deep-tillage rotary blade manufacturing effectively. It is well known that the essence of efficacy losing of rotary blade in operation process is the corrosion wear. Although there have been already a great number of researches on boronizing treatment, they mainly focus on the improvement of wear resistance while corrosion resistance of the surface boronizing layer of boronized 65Mn steel in acid mediums are rarely studied and researches on its corrosion resistance in fertilizer-containing soil (a weak acidic medium) have not been reported at home and abroad so far (Kiratli and Findik, 2011), (Mu et al., 2011), (Guo et al., 2011).

This work focuses on the corrosion behavior of boronized 65Mn steel in two acid mediums and the comparison with the existing technology to ascertain the soil workability of deep-tillage rotary blade made through boronizing treatment.

2. Materials and methods

The 65Mn steel used in the work was manufactured by New Fushun Steel Co., Ltd. of China. The boronizing agent was the powder boronizing agent manufactured by Shandong Jiuxing Heat Treatment Materials Co., Ltd. of China, for which ferroboron and boron carbide were adopted as the boron source and potassium fluoborate as the activator. Size of samples used for the test was 10 mm×10 mm×6 mm. The boronizing temperature was 850 °C and the soaking time was 6 hours. The boronized sample was cleaned for corrosion test.

The corrodent mediums were a strong acidic medium that the hydrochloric solution with 10% mole fraction and a weak acidic medium the fertilizer-containing soil. The soil was from a farmland in Dantu, Zhenjiang, China, being naturally dried in the air, and the fertilizer was 55.9% total nutrient NPK compound fertilizer (N-P_2O_5-K_2O: 11-44-0.09) solution with a 10% mass fraction. The total time of corrosion was 168 hours. During corrosion test, the sample was taken out every other day and weighed with a 1:10,000 electronic balance after being cleaned to calculate the weight variation rate. The weighed sample was put in the changed medium for the next round of test. To obtain uniform corrosion, the sample was put in a nylon string bag and hung in the corrodent. A JSM-7001F field emission scanning electron microscope equipped with an IE-350 energy dispersive spectrometer (EDS) and a LEICA DM2500M optical microscope were employed to observe the surface morphologies and the cross-sectional morphologies of corroded samples.

For the purpose of contrast, the corrosion test was concurrently conducted on 65Mn sample going through 850 °C×0.5h oil quenching plus 210 °C×2h lonnealing.

3. Results and discussion

3.1 Corrosion behaviors in hydrochloric solution

Figure 1 is the corrosion kinetics curves of two samples in the hydrochloric solution, from which it can be observed that the two samples are both in weightless state in the hydrochloric solution, but the weightless speed of

the boronizing-status sample is much lower than that of the lonnealing-status sample. After 168 hours' corrosion, the weightlessness of the boronizing-status sample is only 27.9% of that of the lonnealing-status sample, and this indicates that boronizing treatment can greatly improve the corrosion resistance of 65Mn in hydrochloric solution.

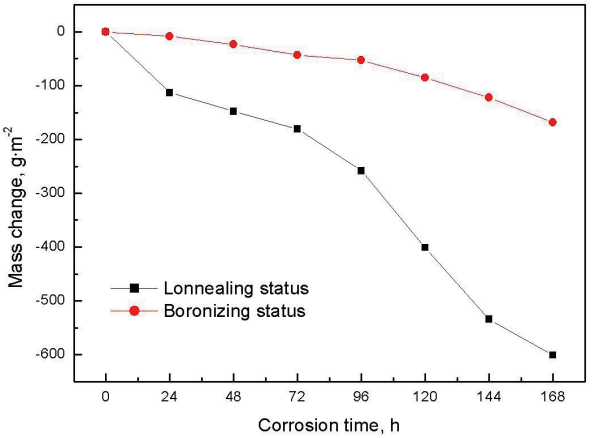

Fig.1. Corrosion kinetics curves of two samples in hydrochloric solution

Figure 2 shows surface SEM morphologies of the two samples after 168 hours' corrosion in the hydrochloric solution, and Figure 2a and 2b respectively represent lonnealing-status and boronizing-status. It can be seen from Figure 2a that, after corrosion, the surface of the lonnealing-status sample is distributed with a great number of large corrosion pits with depth of hundreds of microns (Figure 3a), which shows that the lonnealing-status sample has very poor corrosion resistance in hydrochloric solution and it is mainly subject to pitting corrosion. It can be seen from Figure 2b that, after corrosion, the surface of the boronizing-status sample is only sporadically distributed with small corrosion pits, which shows that the corrosion resistance of boronized 65Mn steel is remarkably improved compared with the lonnealed one, and it is mainly subject to uniform corrosion. It is found in further observation of the cross section of the boronizing-status sample after corrosion (Figure 3b) that, after 168 hours' corrosion in hydrochloric solution, there are only some corrosion areas of few microns found at the interface of the boronizing layer and the substrate of the boronizing-status sample and the surface boronizing layer is still intact and compact.

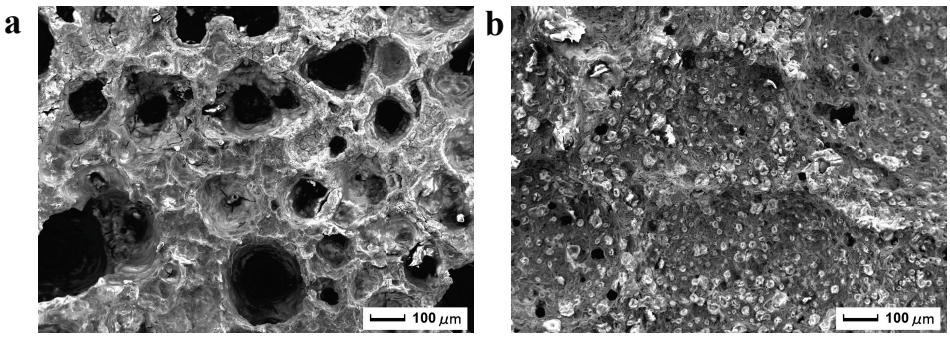

Fig.2. Surface SEM morphologies of two samples after 168 hours' corrosion in hydrochloric solution: (a) lonnealing-status; (b) boronizing-status

According to the general principle of metal corrosion, the corrosion process of metal in acid solution is virtually an electrochemical reaction. H^+ in acid solution clinging on the surface of the metal reverts to be H_2 to get out after obtaining the electrons of metal atoms and the metal losing electrons becomes the anode in electrochemical reaction. The more rapid the metal anodization is, the more intensive the electrochemical reaction is and the weaker the corrosion resistance of the metal is. The lonnealing-status microstructure of 65Mn is a tempered martensite and the Fe atoms on its surface are easy to lose electrons, which leads to rapid anodization, so that it has weaker corrosion

resistance in hydrochloric solution. The surface microstructure of boronized 65Mn is mainly composed of Fe_2B, an intermetallic compound, the Fe atoms of which are difficult in losing electrons and the Fe atoms of substrate after losing electrons have to go through the boronizing-layer before reaching the surface, which significantly reduces the anodization speed, so that it has excellent corrosion resistance in hydrochloric solution.

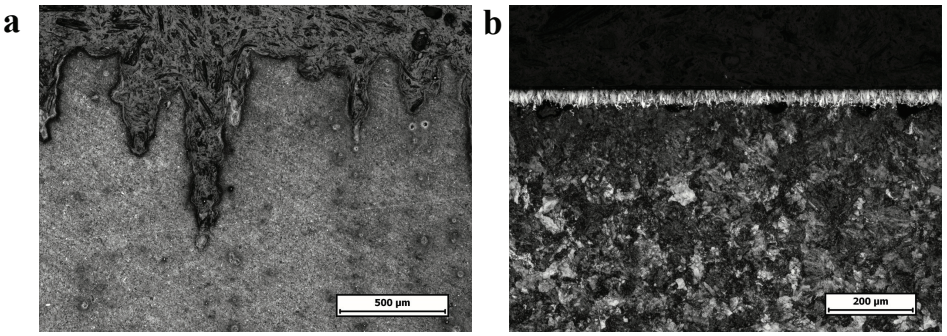

Fig.3. Cross-sectional OM morphologies of two samples after 168 hours' corrosion in hydrochloric solution: (a) lonnealing-status; (b) boronizing-status

3.2 Corrosion behaviors in fertile-containing soil

Figure 4 shows the corrosion kinetics curves of two samples in the fertile-containing soil. As can be seen from Figure 4, weight changes of the two samples in the process of corrosion in the fertile-containing soil also present the same law, i.e. the weight gains and then losses. Wherein， the weight gain of the lonnealing-status sample after 72 hours' corrosion reaches its maximum value (4.49 $g \cdot m^{-2}$), but in the next around 100 hours' corrosion, weight loss happens to the sample at a relatively high rate, and after about 150 hours' corrosion, its weight becomes lighter than the original one. The weight gain of the boronizing-status sample also reaches its maximum value (3.72 $g \cdot m^{-2}$) after 96 hours' corrosion, however, which is smaller than that of the lonnealing-status sample, then the weight loss happens at a relatively low rate during 96-144 hours' corrosion, and in the next 24 hours' corrosion, it shows weight gain again. These results suggest that the corrosion resistance of the boronizing-status sample in fertile-containing soil is much better than that of the lonnealing-status sample.

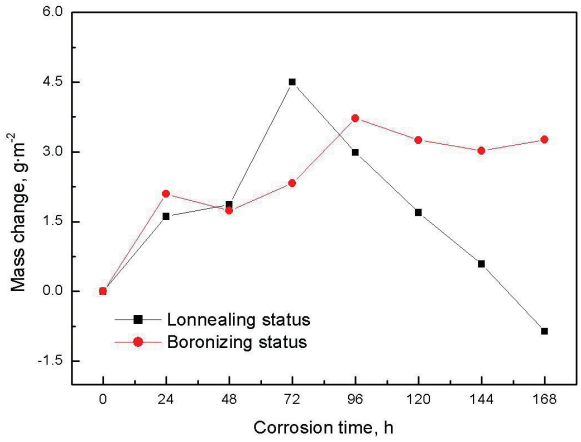

Fig.4. Corrosion kinetics curves of two samples in fertilizer-containing soil

Figure 5 shows the surface SEM morphologies of the lonnealing-status sample after 168 hours' corrosion in the fertilizer-containing soil, in which Figure 5a, b and c respectively present low magnification morphology, high magnification morphology and EDS energy spectrum of zone A. As can be seen from Figure 5a, after 168 hours'

corrosion in the fertilizer-containing soil, the surface of lonnealing-status sample suffers severe peeling. There are many different sizes peeled areas distributed on the surface, among which small peeled areas appear to be spherical or near-spherical and take on "crack" feature at the bottom and all around (Figure 5b). Further EDS analysis of the minor peeled areas finds that the main components in the areas are Fe, O and P (Figure 5c). The analysis deems that, at the initial stage of corrosion, a phosphating reaction occurs when Fe on the surface of lonnealing-status sample comes into contact with the orthophosphoric acid which is formed by NPK compound fertilizer whose main component is P_2O_5 upon dissolution in water. Moreover, H_2, as one of reaction products of such reaction, is absorbed on the surface of the sample. As there is no oxidized accelerator which is normally used in phosphate treatment to eliminate H_2 on the sample surface, only Fe is dissolved without formation of phosphate film. As time goes by, $Fe(H_2PO_4)_2$ layer, another phosphating reaction product, constantly thickens, and cracks are formed under the action of the growth stress. At the same time, the orthophosphoric acid in the soil penetrates into the substrate via the cracks and has the above mentioned phosphating reaction with the substrate, which makes the local phosphating reaction product $Fe(H_2PO_4)_2$ layer thicker and then causes the layer peel off. Based on the above analysis, it is not difficult to explain the law that the lonnealing-status sample loses weight after gaining weight both at a rapid rate in the corrosion kinetics curve.

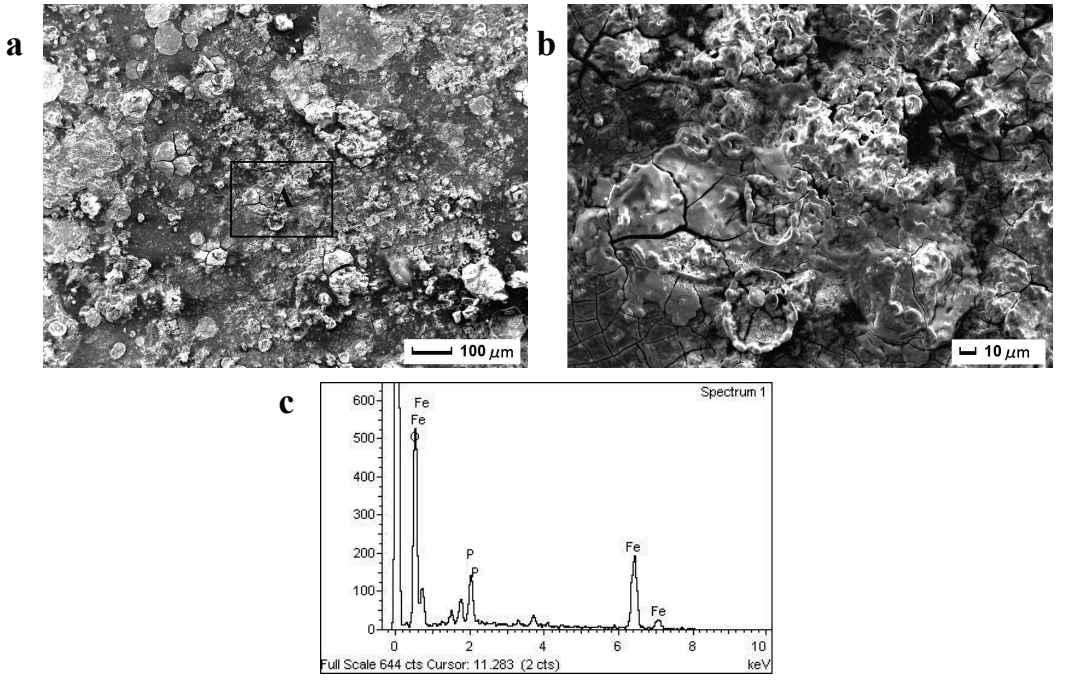

Fig.5. Surface SEM morphologies of lonnealing-status sample after 168 hours' corrosion in fertilizer-containing soil: (a) low magnification morphology, (b) high magnification morphology, (c) EDS energy spectrum of zone A in Fig.5a

Figure 6 shows the surface SEM morphologies of the boronizing-status sample after 168 hours' corrosion in the fertilizer-containing soil, in which Figure 6a and 6b respectively present low magnification morphology and high magnification morphology, and Figure 6c and 6d respectively present EDS energy spectrums of zone A and zone B. As can be seen from Figure 6, after 168 hours' corrosion in the fertilizer-containing soil, two different morphologies emerge on the surface of the boronizing-status sample wherein gray areas mottled with white spots are the structure with white acicular microstructure distributed on the substrate featured by "crack" (Figure 6b). A further EDS analysis indicates that the main components are Fe, O and P (Figure 6c), which are same to the surface components of the lonnealing-status sample corroded in the fertilizer-containing soil, but its P content is obviously higher than that of the lonnealing-status sample after corrosion. According to the results of Section 3.1 in this work, in acidic mediums, the corrosion resistance of the boronizing-status sample is much stronger than that of the lonnealing-status.

Therefore, it can be inferred that, although similar to the lonnealing-status sample, the boronizing-status sample enters into a phosphating reaction with orthophosphoric acid in the fertilizer-containing soil, but its extent is much lower than that of the lonnealing-status sample. The remaining orthophosphoric acid, after dehydration, is deposited on the sample surface in the form of white acicular microstructure. Combined with the corrosion kinetics curves, the weight gain of the boronizing-status sample in the fertilizer-containing soil at the early stage of corrosion is the result of the mild phosphating reaction and the deposition of P_2O_5. A further EDS analysis of the black areas on the surface of boronizing-status sample indicates that the main components of the area are Fe, Mn and S, without P (Figure 6d). Meanwhile, the black areas take on a feature of looseness, which is similar to the morphology of the boronizing-status sample. It can be inferred that, the black areas on the surface of the boronizing-status sample are non-corroded boronizing microstructures.

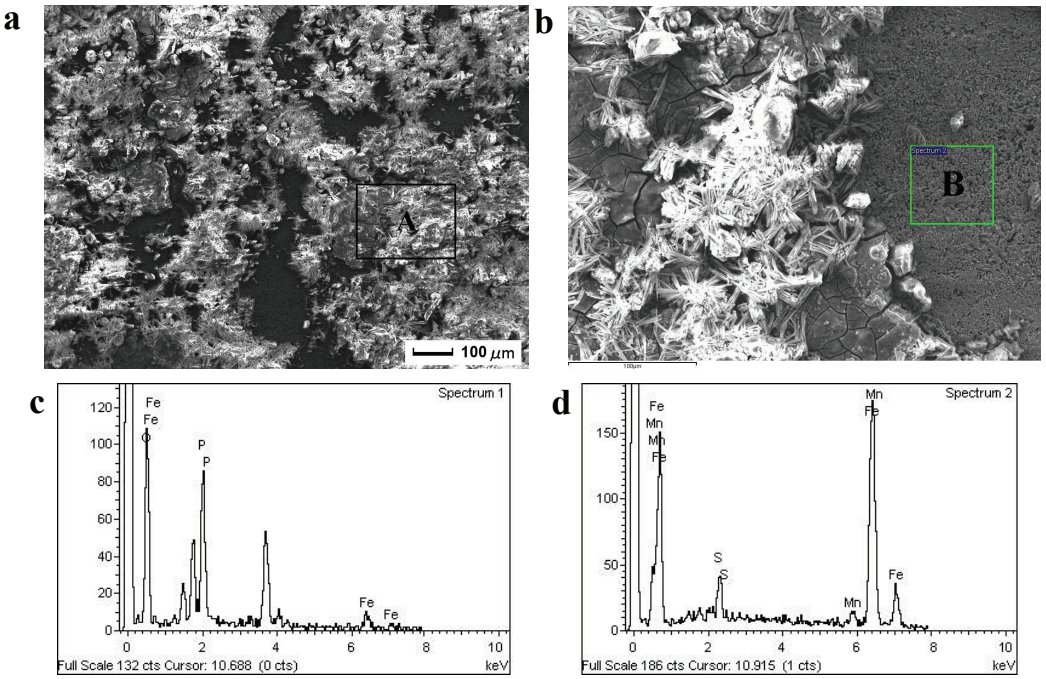

Fig.6. Surface SEM morphologies of boronizing-status sample after 168 hours' corrosion in fertilizer-containing soil: (a) low magnification morphology; (b) high magnification morphology; (c) EDS energy spectrum of zone A in Fig.6a; (d) EDS energy spectrum of zone B in Fig.6b

Figure 7 presents the cross-sectional OM morphologies of the two samples after 168 hours' corrosion in the fertilizer-containing soil, wherein Figure 7a and 7b respectively present the morphologies of the lonnealing-status and the boronizing-status. As can be seen from Figure 7, there are lots of corrosion pits in the surface of the lonnealing-status sample after 168 hours' corrosion in the fertilizer-containing soil; while the boronizing layer on the surface of the boronizing-status sample is still intact and compact, and no corrosion evidence is found at interface of the boronizing layer and the substrate. The above results indicate that after boronizing treatment, the boronizing layer on the surface of 65Mn steel effectively resists the corrosion of fertilizer-containing soil, thus the corrosion resistance of 65Mn steel is improved prominently.

4. Conclusions

(1) After 168 hours' corrosion in the hydrochloric acid solution, the weight loss of the boronizing-status sample is only 27.9% of that of the lonnealing-status sample. The surface of the boronizing-status sample is only sporadically distributed with small corrosion pits, while the surface of the lonnealing-status sample is distributed with a large number of large corrosion pits with a depth of hundreds of microns.

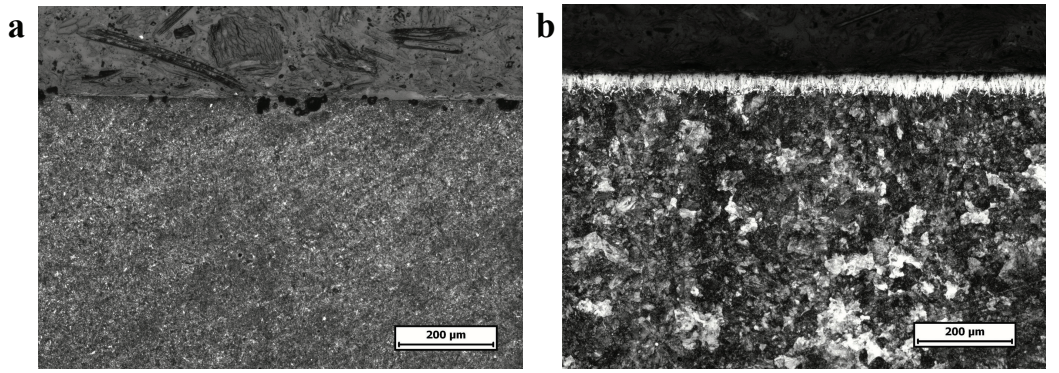

Fig.7. Cross-sectional OM morphologies of two samples after 168 hours' corrosion in fertilizer-containing soil: (a) lonnealing-status, (b) boronizing-status

(2) After 168 hours' corrosion in the fertilizer-containing soil, there is no obvious weight loss in the boronizing-status sample, while the weight of the lonnealing-status sample is lighter than the original weight after about 150 hours' corrosion. Meanwhile, the surface of the boronizing-status sample is still intact and compact and no obvious corrosion feature is found, while the surface of the lonnealing-status sample suffers severe peeling.

(3) Although the corrosion kinetics curves of the two samples in acid mediums show the same law, the corrosion resistance of 65Mn steel subject to the boronizing treatment has been obviously improved both in the hydrochloric solution and in the fertilizer-containing soil compared with that treated with the lonnealing treatment after overall quenching.

(4) The improvement of corrosion resistance of 65Mn steel after boronizing treatment lies in that boronizing treatment significantly reduces the anodization speed of steel in strong acid medium and effectively prevents the phosphating reaction of steel in weak acidic medium.

Acknowledgements

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